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Title: Improved Hydrogen Getter Materials: FY17 Activities for the Enhanced Surveillance and Readiness Campaigns

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Improved Hydrogen Getter Materials:

FY17 Activities for the Enhanced Surveillance and Readiness Campaigns

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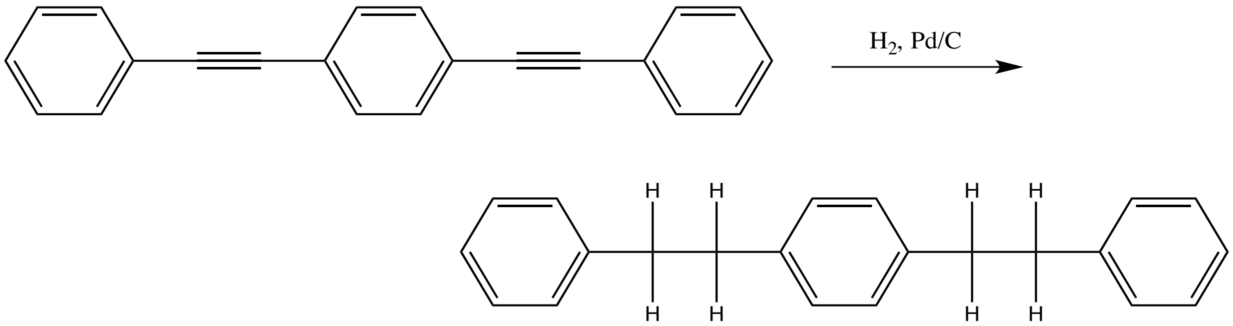
Denisse Ortiz-Acosta and Tanya Moore (C-CDE)

January 30, 2018

Introduction



- Material under study is a catalyst/getter composite
  - Pd organometallic compound – catalyst for H_2 dissociation
  - DEB – irreversible organic hydrogen getter
- Getter composite can be infiltrated into the pore structure of open-celled foams by vapor- or solution-phase methods
  - High surface area
  - Direct contact with emitting or sensitive materials
  - Direct replacement of existing materials

- Study of manufacturing issues need to be addressed to better inform any potential decision on production

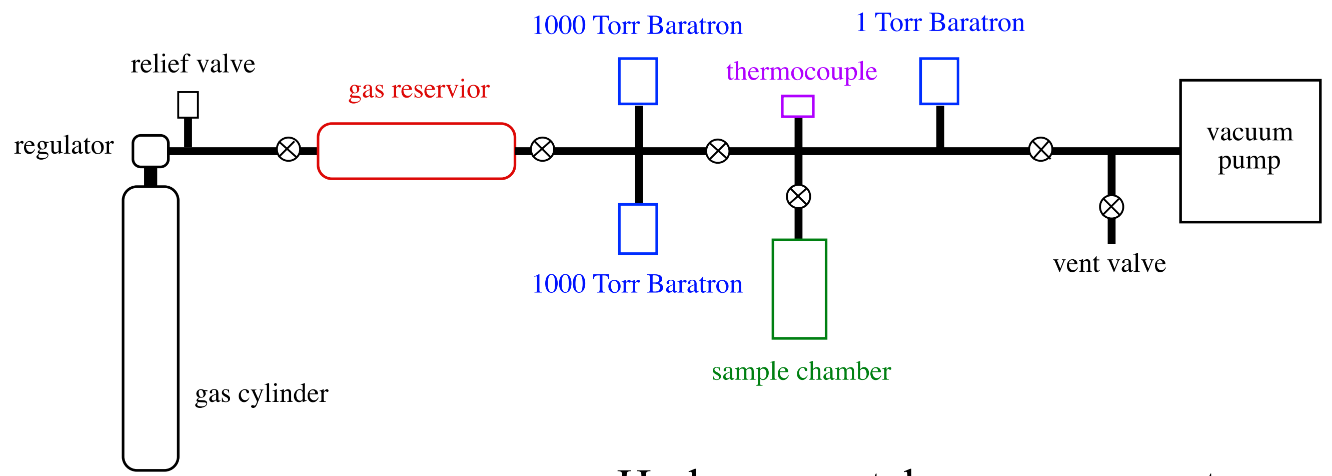
FY17 Tasks

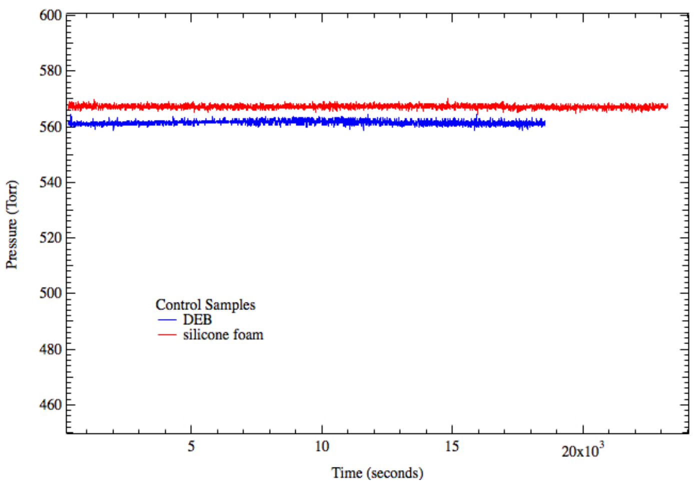
- Vapor phase deposition:
  - Improve sublimation stability (with time) and efficiency for DEB deposition
  - Analyze volatile species present in getter/catalyst deposit
    - Effect of hydrogenation
    - Effect of UV exposure during deposition

- Solution phase deposition:
  - Evaluate:
    - Reproducibility
    - Solution aging
    - Solution re-use
  - Develop proof-of-principle concept for infiltration of multiple substrates
  - Develop a concept for recycling of toluene solvent

- Additive manufacturing of silicone/getter composites (C-CDE collaboration funded by Enhanced Surveillance, but of relevance to Readiness):
  - Examine getter performance as a function of resin composition, curing temperature, and catalyst type
  - Demonstrate printing of 3D structures (C-CDE)

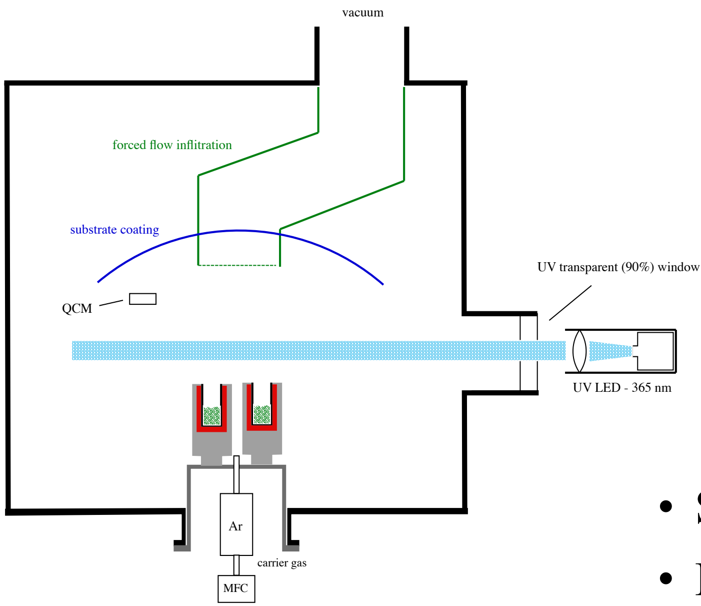
Characterization

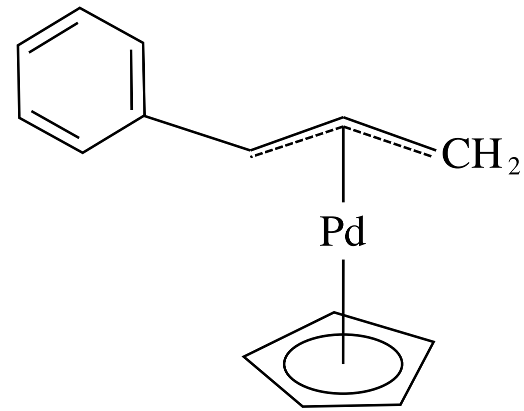




- Hydrogen uptake measurements
  - p,T vs t in a closed system
    - Not realistic conditions - screening
    - Confirmed lack of reaction with pure DEB or pristine silicone
- IR spectroscopy
- Thermal analysis (DSC/TGA)
- SEM/EDS
- RBS (composition)

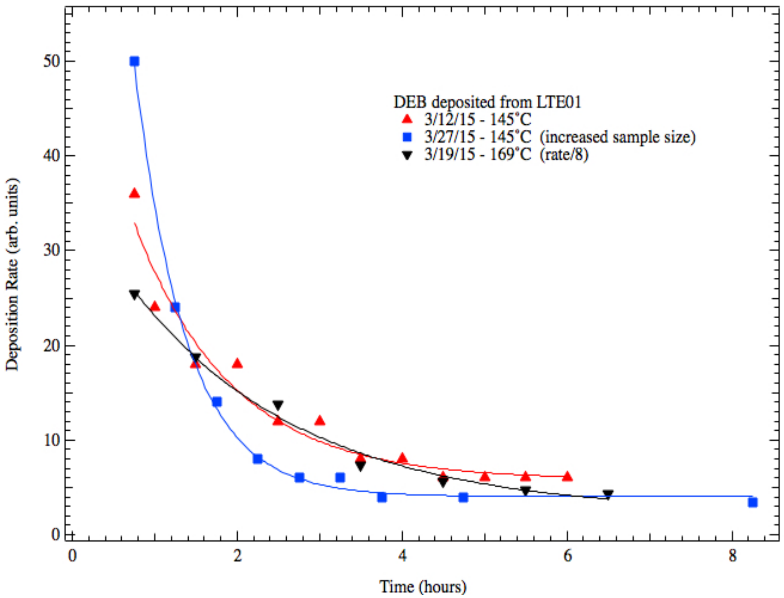
Vapor Deposition Process

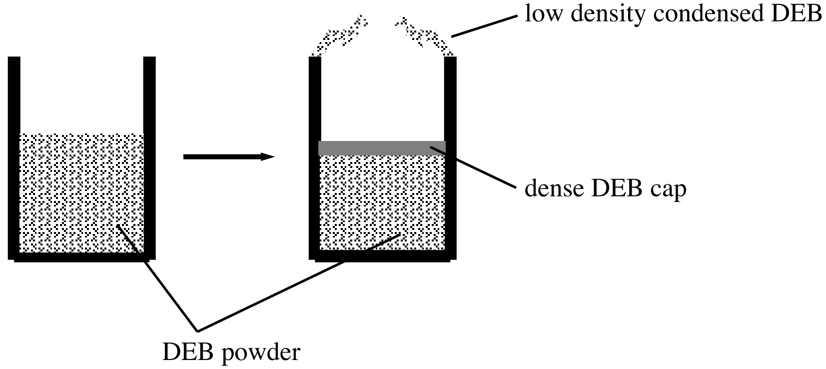




- Sublimation of DEB
- Evaporation of Pd organometallic precursor
  - Cyclopentadienyl[(1,2,3-n)-1-phenyl-2-propenyl]Pd
    - Optional photolysis with UV LED (365 nm) – 50 mW/cm^2 (aging/compatibility)
  - M97xx foam sheets from KCP (1-3 mm thick)
  - Forced-flow substrate configuration
  - 1-2 wt% loading

DEB Deposition Rate

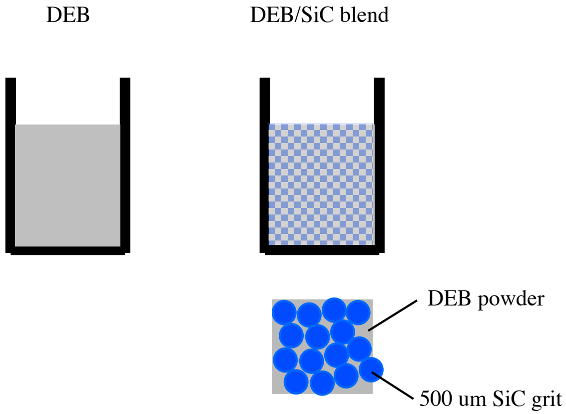


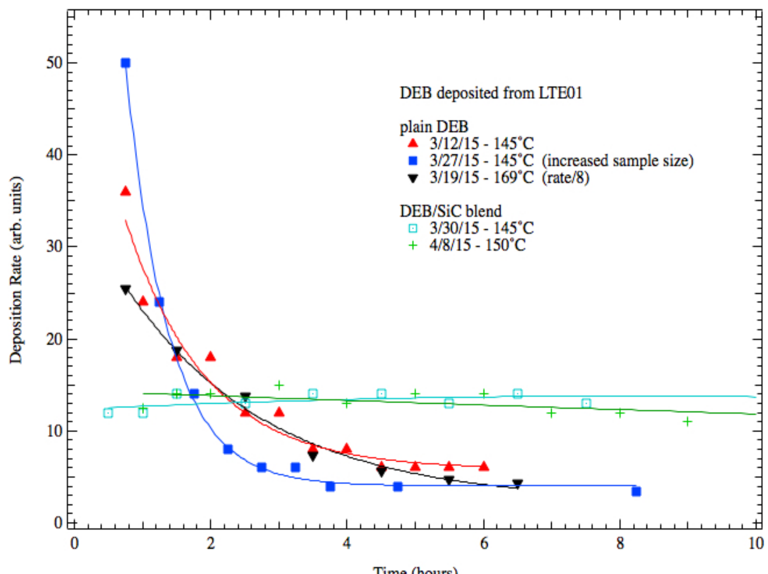


- Sublimation/deposition rate of DEB decreases very quickly with time
  - Difficult to control deposit composition (DEB/Pd ratio)
  - Limits film thickness
- Grain coarsening
  - Decrease in specific surface area
  - Formation of dense "cap"
- Re-condensation
  - Forms a low-density, filamentary, "trap" above the crucible

Small-Scale Solution

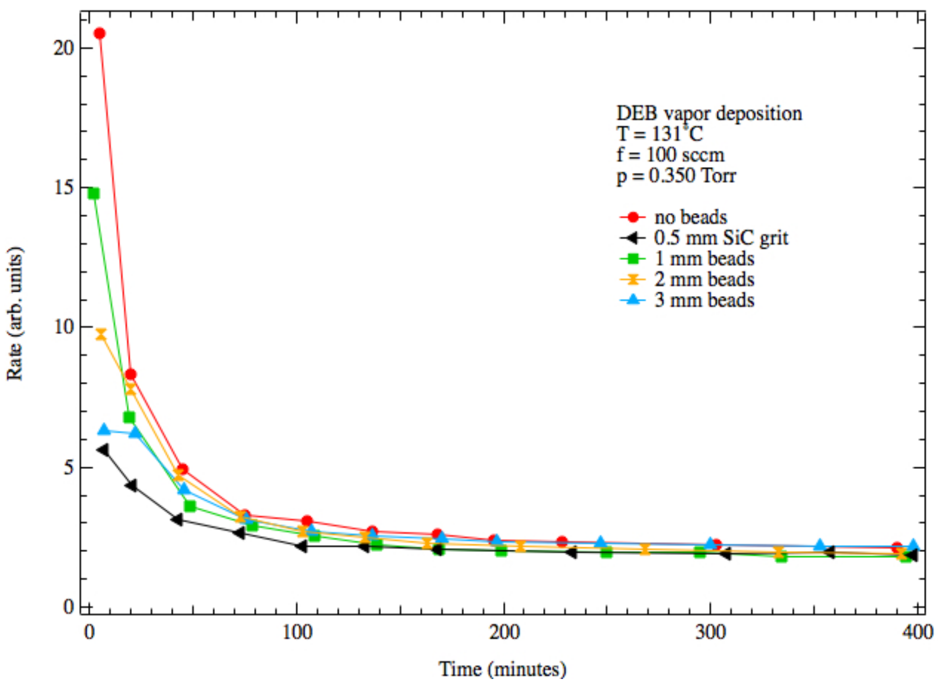
L.W. Fannin, D.W. Webb, and R.H. Pearce, J. Cryst. Growth **124** (1992) 307





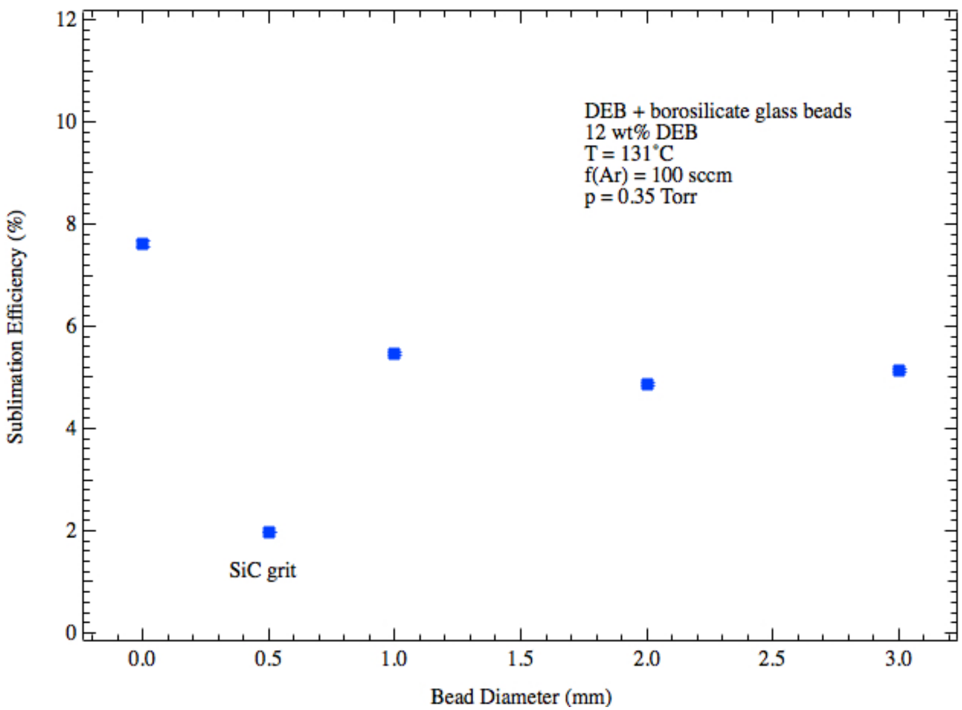
- Blend DEB with SiC grit
  - DEB present in "interstitial" volume
  - Limits grain coarsening
- Added a supplementary ring-shaped heater near the crucible rim
- Work in FY16 demonstrated reasonable success using a small (1cc) source
  - Uniform deposition rate
  - Little re-condensation at crucible lip

Large-Scale Solution Attempt



- For FY17 it was attempted to implement this solution using a larger DEB source with a 10cc crucible – necessary to enable deposition over larger surface area and/or multiple substrates
  - SiC grit
  - Glass beads of various sizes (1-3 mm)
- This approach was not successful for the larger source
- Deposition rate still decreases quickly with time

Deposition Efficiency



- Also, sublimation efficiency is quite low and is made worse by use of the grit/beads

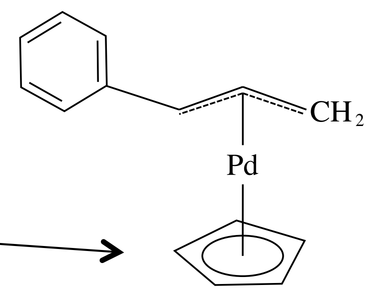
- Reasonable coating thickness can actually still be obtained with the larger 10cc source, at least for small substrates

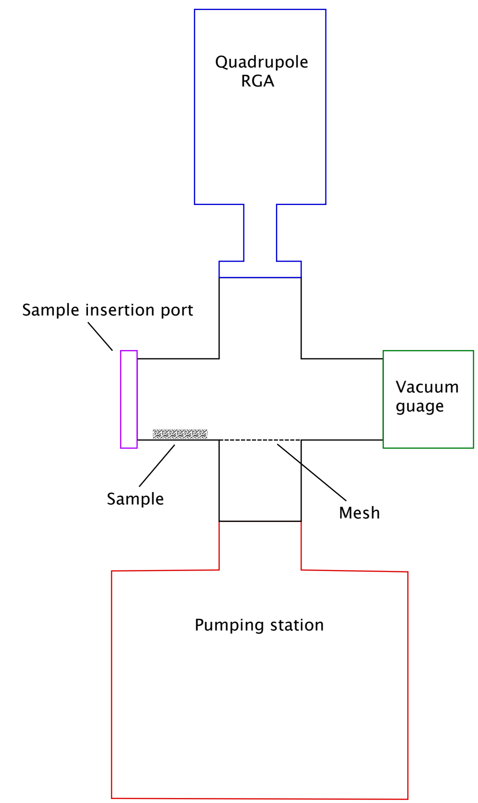
- However the process is very wasteful of DEB – material recovered from the crucible can probably not be re-used because of grain coarsening that would reduce sublimation rate

Analysis of Volatile Species

- Getter samples produced by vapor-phase infiltration clearly contain volatile organic species
- May be an issue with respect to long-term aging and compatibility

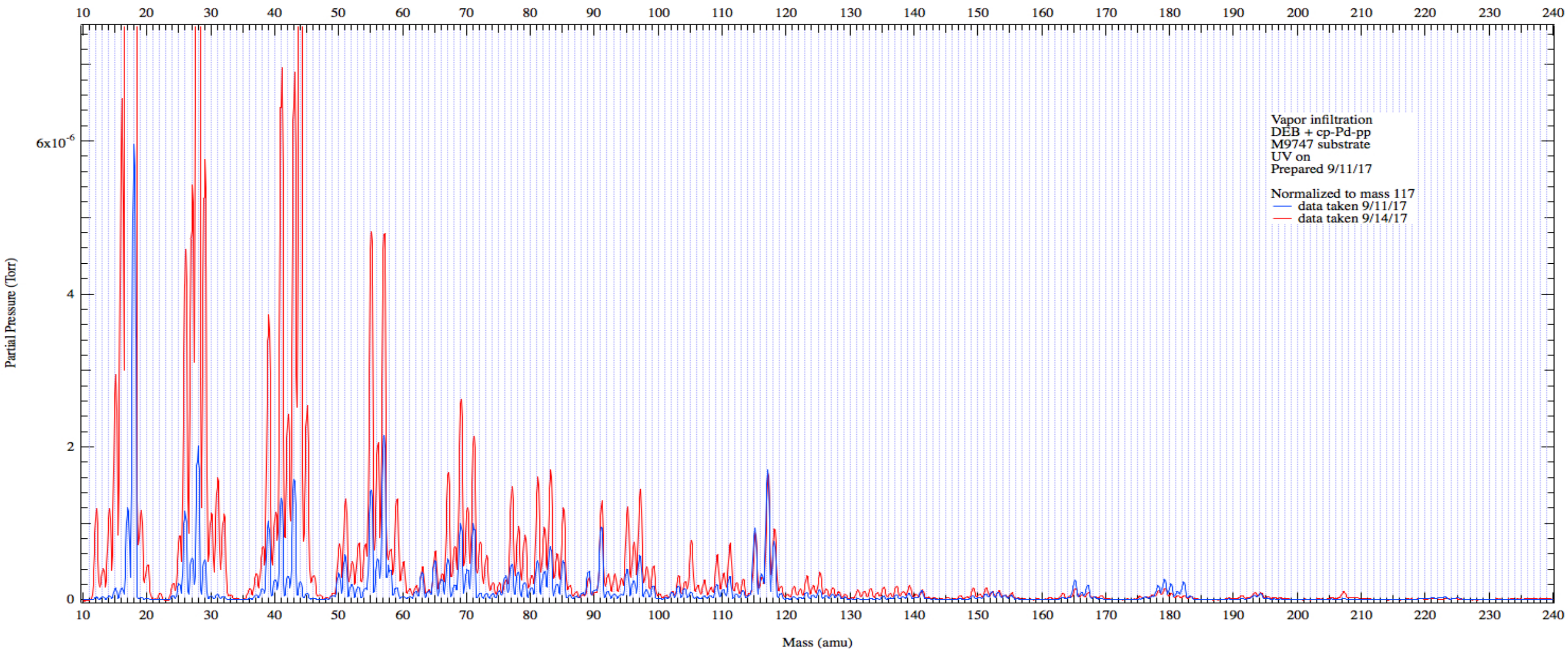
- Attempt to identify species using an RGA
  - Phenylpropenyl-based
  - Cyclopentadienyl-based





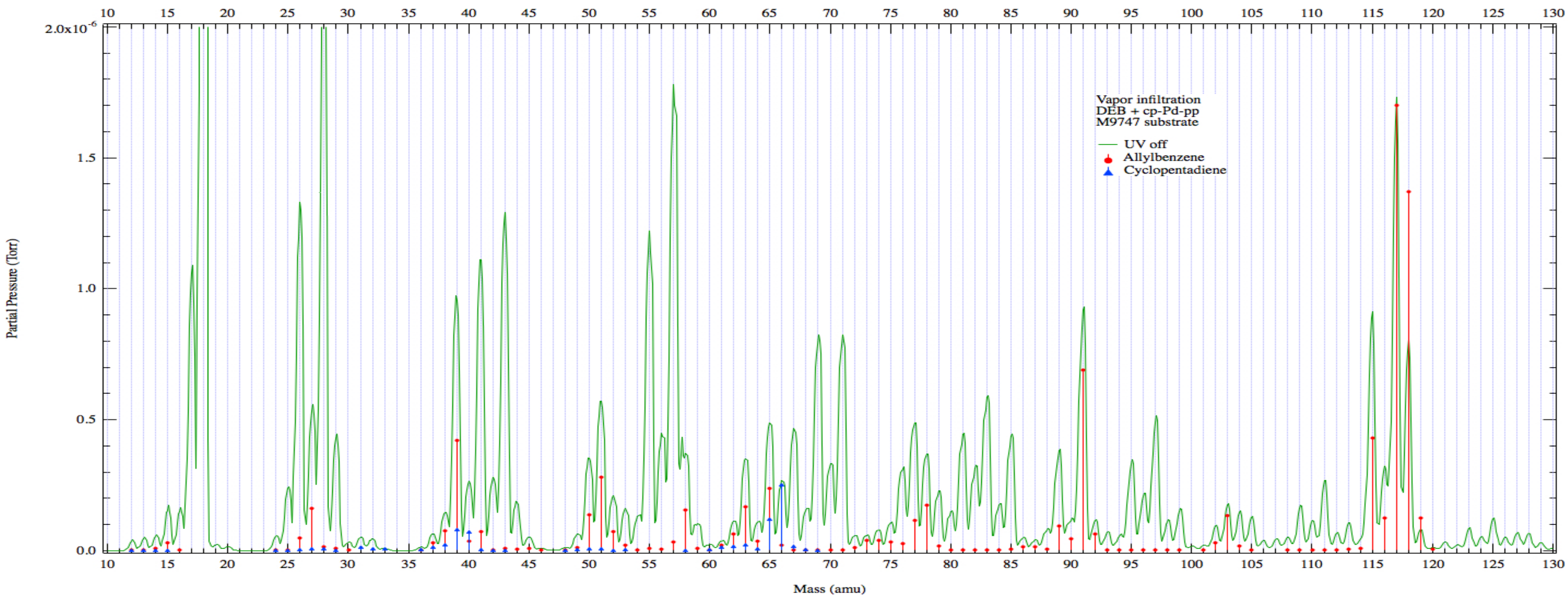
- Effect of UV exposure during infiltration
  - 25 mW/cm^2 directed through cp-Pd-pp vapor plume

Volatile Species – Time Dependence



- Data indicate that much of the volatile species are significantly depleted over a period of days
  - Exception is 115-118 amu – phenylpropenyl-based species
  - Only two data points, so a "half-life" was not determined

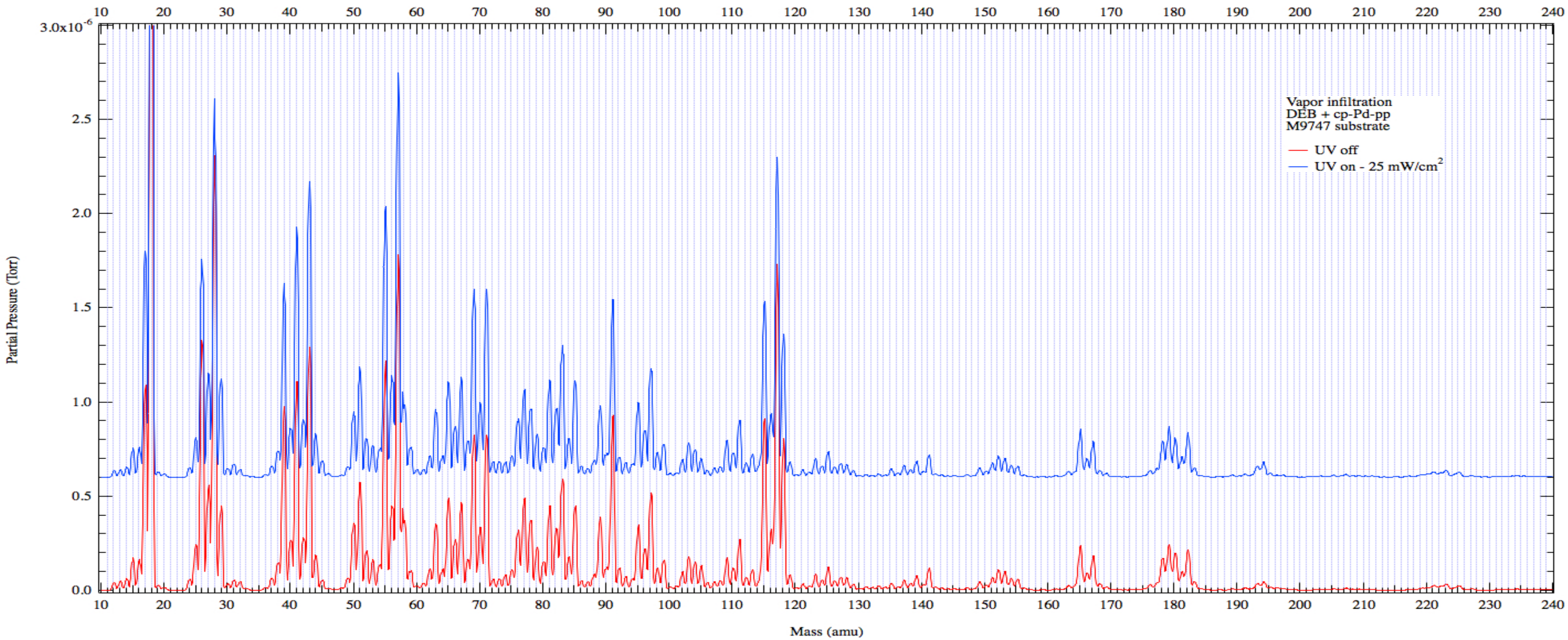
Volatile Species – Composition



- Phenylpropenyl-based species can clearly be identified
  - Remains largely intact during the deposition process
  - Incorporated into the growing film, either still bound to Pd or otherwise

- Cyclopentadiene-based species are not clearly identified
- Most of the peaks can not be clearly associated with either of the two ligands
  - Significant fragmentation, reaction of the Cp ligand

Volatile Species – Effect of UV Exposure



- Exposing the cp-Pd-pp vapor plume to UV during exposure has no effect on the volatile species present in the deposit
  - UV does not induce additional fragmentation/reaction of the precursor
    - Flux or photon energy too low??
    - May require sustained illumination of the substrate – not practical for a production system

Vapor Infiltration - Summary

- Grain coarsening causes the sublimation/deposition rate of DEB to decrease quickly with time
  - A solution adopted from the semiconductor industry was effective for a small DEB source, but not for the larger source that would be needed to infiltrate larger and/or multiple substrates
- However, deposition of the Pd precursor also decreases with time (due to decomposition of the compound in the source), so that the variation in deposit composition with time is manageable
  - Both sources were therefore be used as-is in order to continue evaluation of the effects of UV exposure during deposition, and to analyze volatile species in the deposit

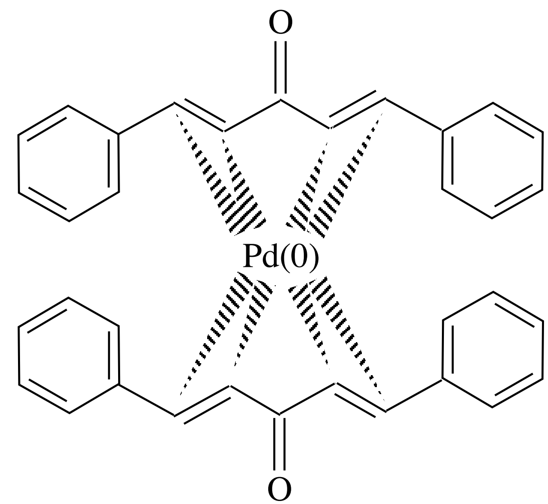
- Volatile species from the getter deposit were readily detected and analyzed
- Phenylpropenyl-based species can be identified
  - This ligand largely remains intact during deposition and is relatively non-volatile
  - It is deposited in the growing film, either still weakly bound to the Pd or in isolation
- Cyclopentadienyl-based species are not identified, and....
- Most of the observed species can not be specifically associated with either of the two ligands present in the original precursor
  - The Cp ligands may have largely fragmented/reacted during deposition and been deposited as a relatively volatile mix of organic species in the growing film
  - The concentration of this organic mix (but not of the phenylpropenyl species) decreases noticeably over a period of days, but a "half-life" was not determined

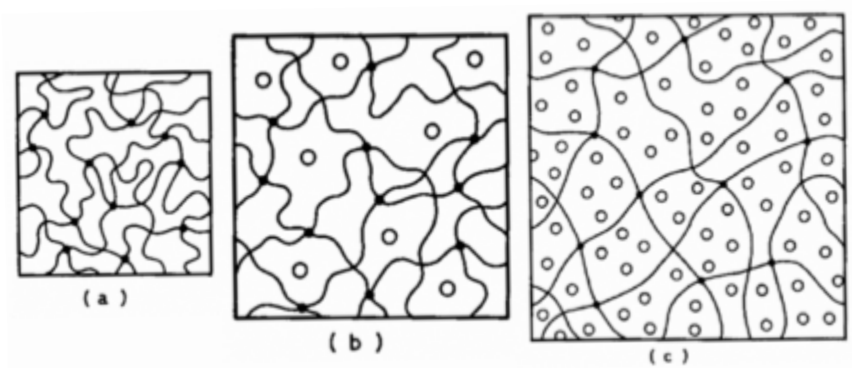
Solution Deposition Process

- Eliminate complex vacuum system
- More uniform infiltration
- Higher loading

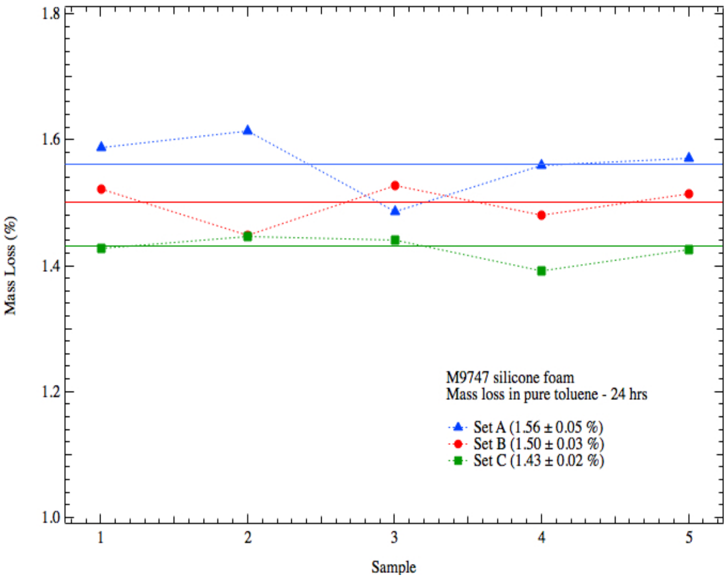
- DEB
- Bis(dibenylidenenacetone)Pd(0)
- Toluene
  - Good solubility – intimate mixing
  - Swelling ratio = 1.3 (Lee et al., Anal. Chem. **75** (2003) 6544)
    - Ability to infiltrate at a molecular level
    - Slight (~10%) degradation in mechanical properties

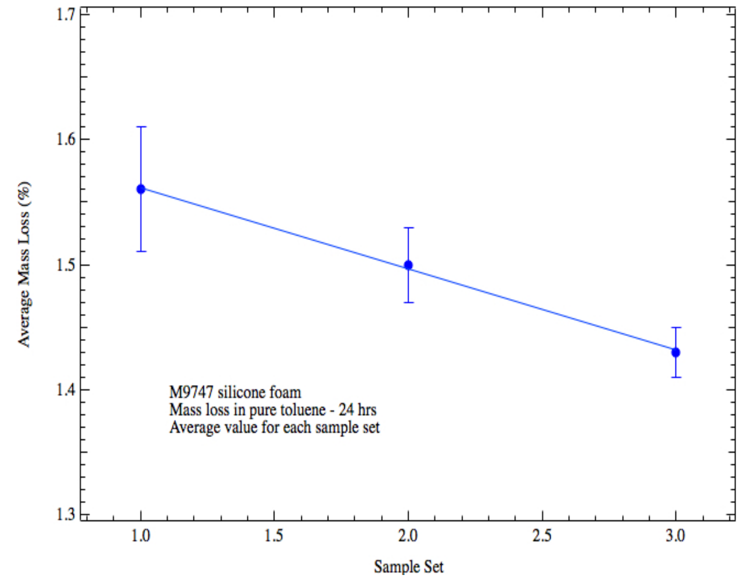
- Mix solution
- Immerse M9747 foam for 24 hours
- Remove foam and evaporate solvent (ambient)
- 3-8 wt% loading





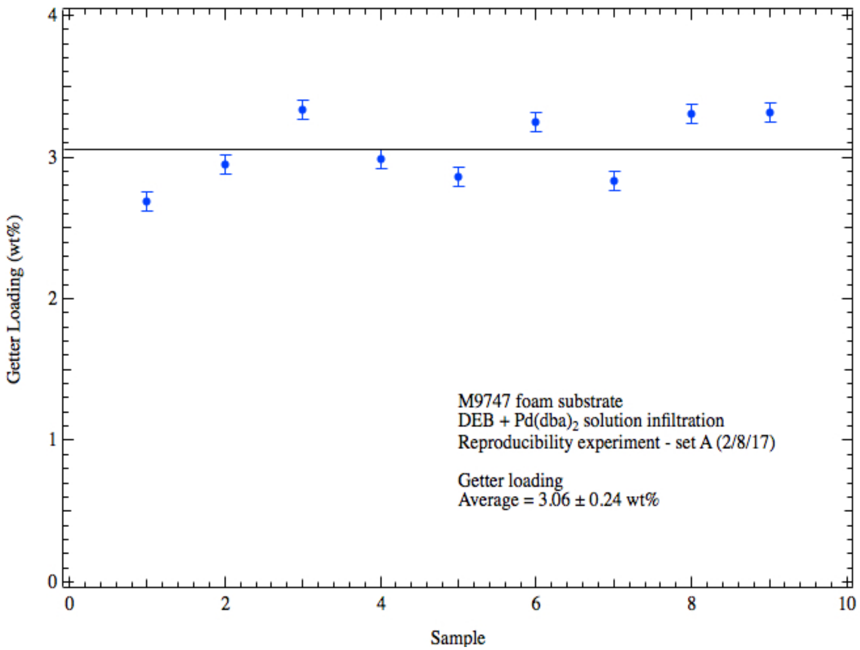
Toluene/Silicone Interaction





- Toluene extracts unpolymerized monomer from the M9747 silicone foam
  - Resulting mass loss makes it difficult to quantify getter loading
- It is necessary to measure the foam mass loss in *pure* toluene so that getter loading can be accurately determined by measuring foam mass before/after infiltration
  - Average mass loss is 1.56 ± 0.05 wt% for 24 hour immersion
  - Mass loss decreases slightly as toluene is re-used
    - Is toluene starting to become saturated?

Process Reproducibility - Loading

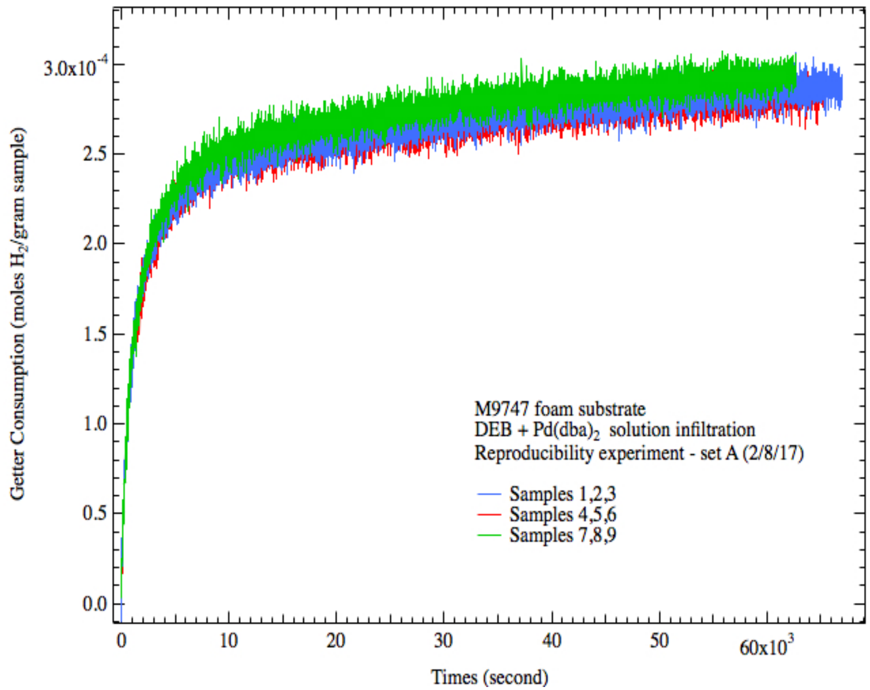


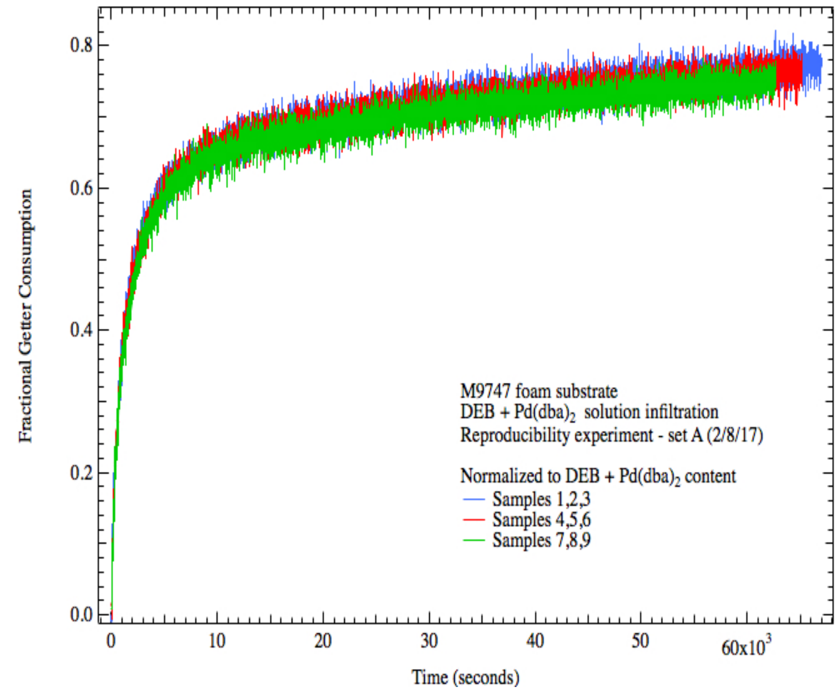
- Loading of 3.06 wt% nominally provides a capacity of 0.038 mole H_2 = 0.84 L H_2 per 100 grams of foam
- Previous experiments show loading can be easily increased by increasing solution concentration or foam specific surface area

- Nine samples were prepared from nine nominally identical solutions
  - Average loading is 3.06 ± 0.24 wt%
  - Sample-to-sample variation is greater than the uncertainty in the loading measurement
    - Will be necessary to define an acceptable range

- Infiltration nominally consumed 3.7 ± 0.4 wt% of the precursor from solution
  - Limits potential solution re-use
  - Could be reduced by increasing the ratio of solution volume to sample size, though this would increase solvent usage

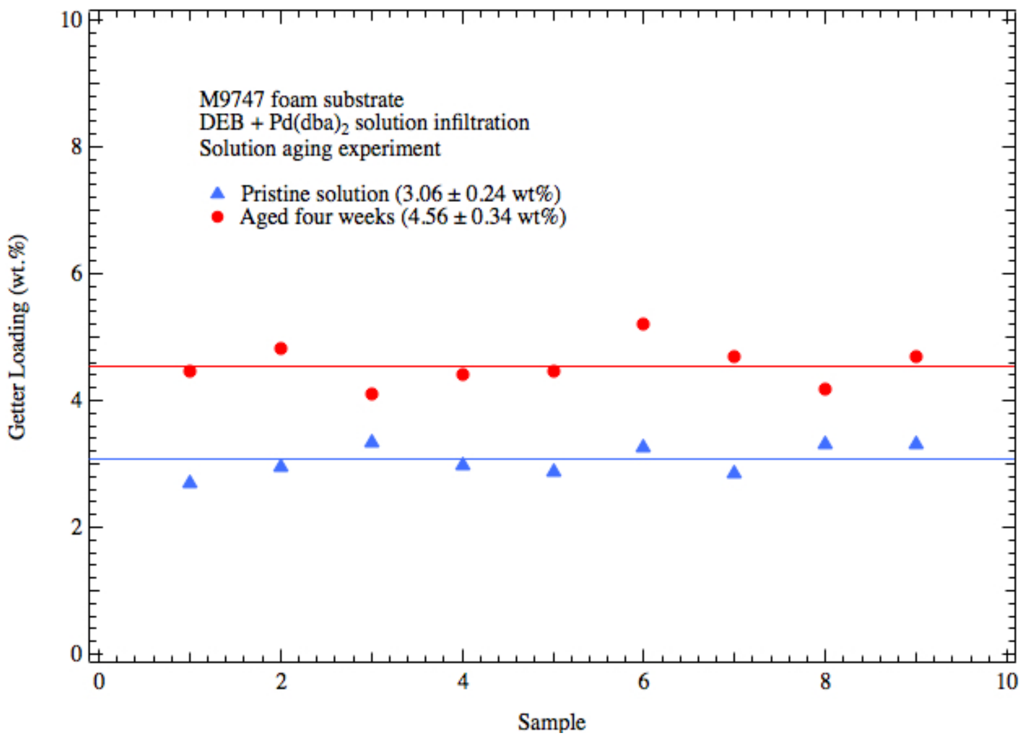
Process Reproducibility - Performance





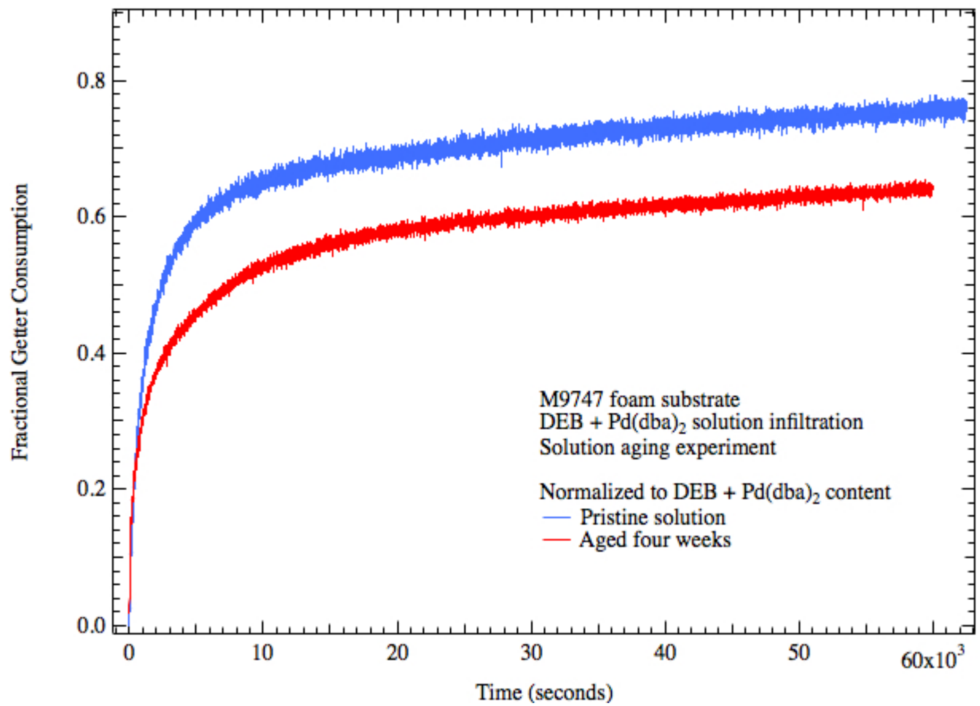
- Hydrogenation of the infiltrated samples was measured as a function of time
- Three sets of three samples each to improve S/N
  - Data show very good reproducibility
  - Reaction extent confirms hydrogenation of the $Pd(dba)_2$ precursor
  - Overall reaction proceeds to 80 ± 3% assuming DEB and $Pd(dba)_2$ are deposited and hydrogenated with equal efficiency

Solution Aging - Loading



- Nine jars of nominally identical solution were prepared and aged for four weeks - ambient temperature with magnetic stirring
- Nine foam samples were infiltrated using the aged solution
  - Pristine: 3.06 ± 0.24 wt%
  - Aged: 4.56 ± 0.34 wt%
- Significant *increase* in loading!

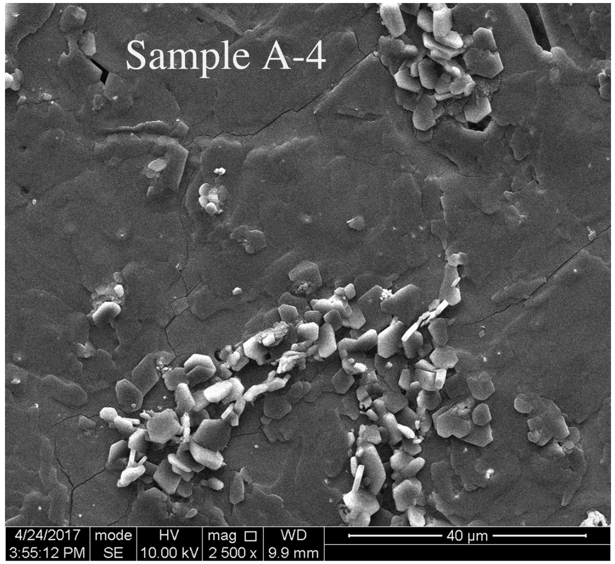
Solution Aging - Performance



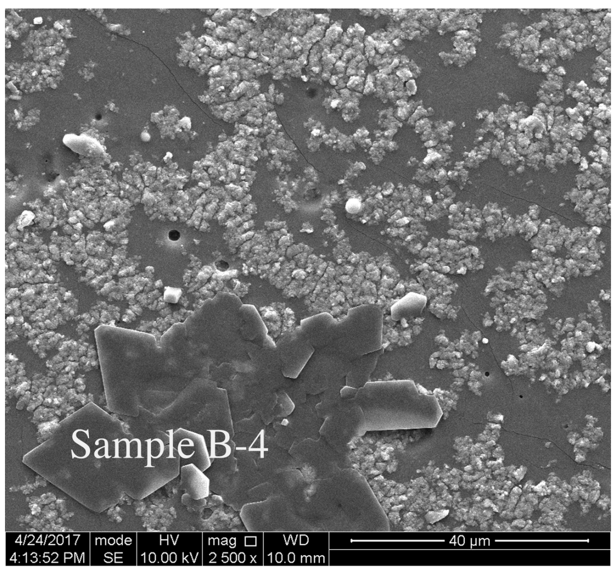
- Hydrogenation data were obtained as a function of time for samples prepared from pristine and aged solutions
- Consumption data normalized to getter content (fractional getter consumption) indicate significant differences in deposit properties
  - Morphology, composition, chemistry…

Solution Aging – Deposit Structure

Pristine solution



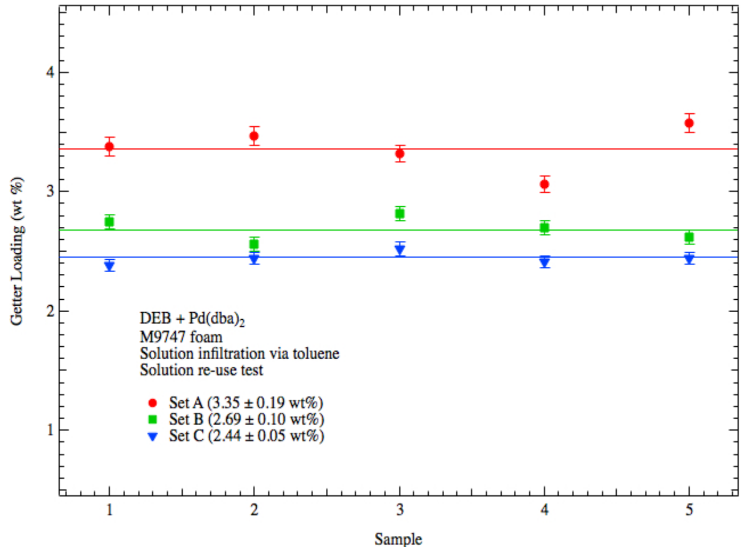
Aged solution

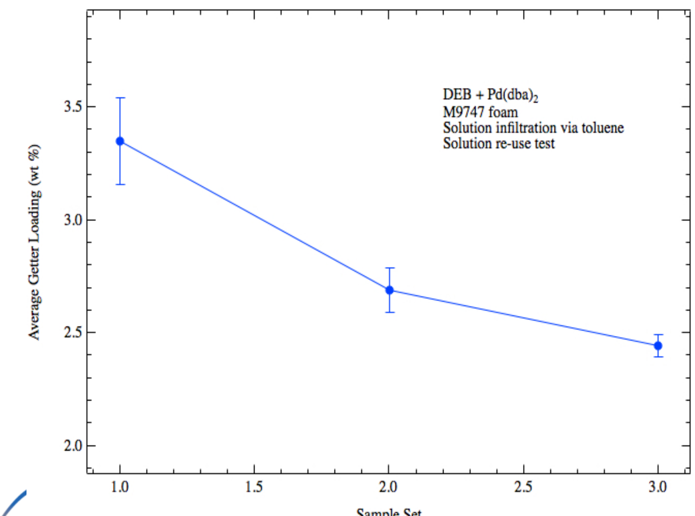


- Deposits prepared from the aged solution show a high concentration of micron-scale nodules
- It is speculated that these modules are, or contain, metallic Pd

- Pd(dba)$_2$ is known to gradually (days-weeks) decompose in toluene to form Pd nano/micro-particles and free dba ligand
  - Consistent with solution color change from red/purple to black
- Resulting variations in particle concentration and solution composition would alter the deposit characteristics and could account for the observed changes in loading and performance

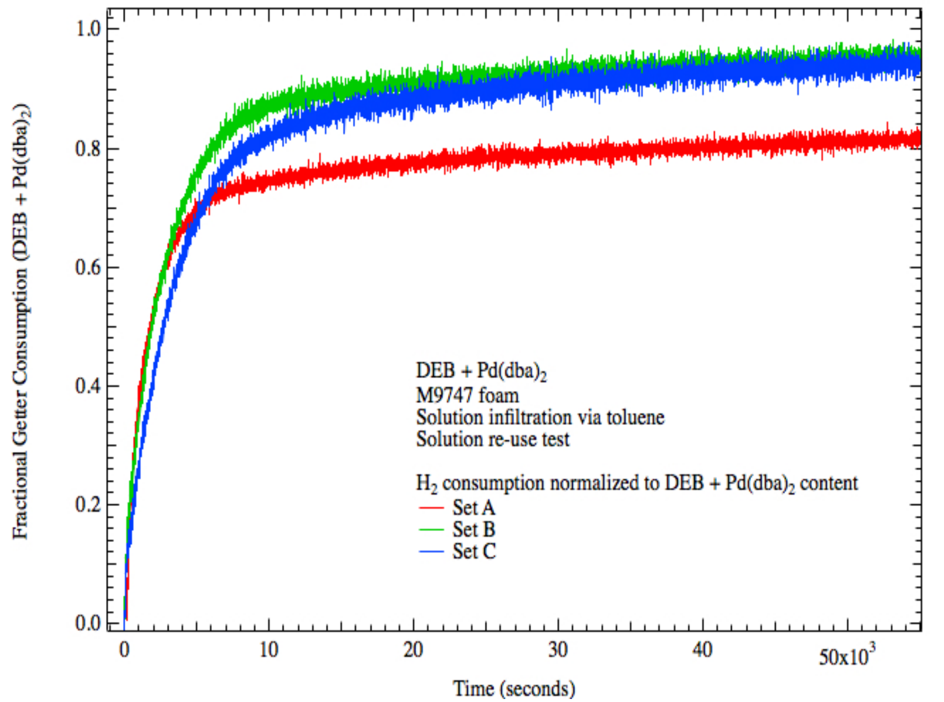
Solution Re-Use - Loading





- Five jars of nominally identical solution were prepared
- Three sets of five samples each were prepared on successive days
  - Minimizes effects of solution aging
- Loading was found to progressively decrease from set-to-set
  - 3.35 → 2.69 → 2.44 wt%
  - Especially for sets 1 and 2, the difference is much greater than can be accounted for by the depletion of precursor in the solutions.
  - Note that sample-to-sample variation also decreases progressively

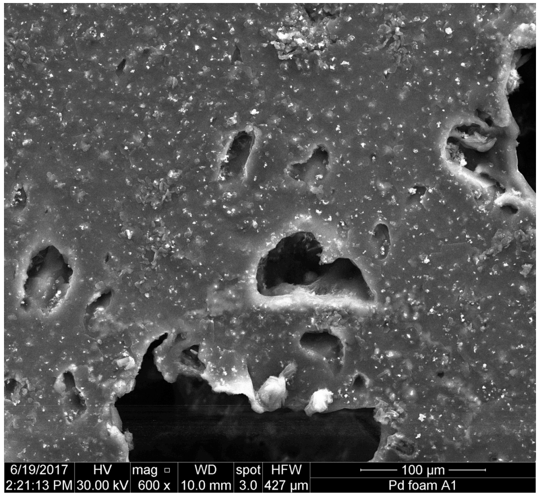
Solution Re-Use - Performance



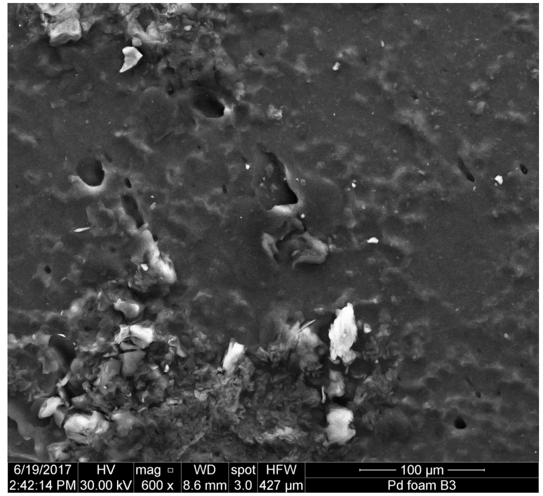
- Hydrogenation data for the samples was measured as a function of time
  - All five samples from a given set were measured simultaneously to improve S/N
- Significant variations are again observed when the hydrogen consumption data are normalized to getter content
  - Significant differences in deposit properties
    - Morphology, composition, chemistry…

Solution Re-Use - Structure

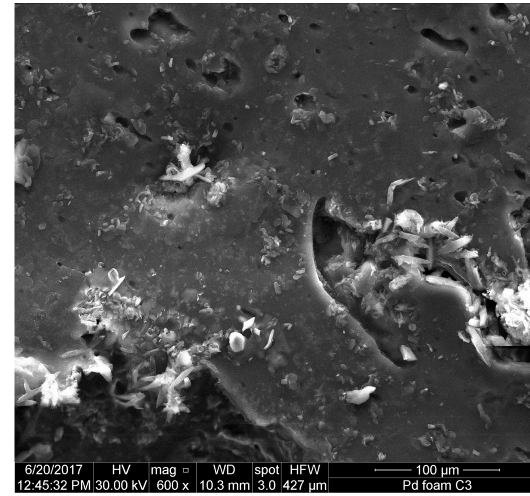
Set 1



Set 2

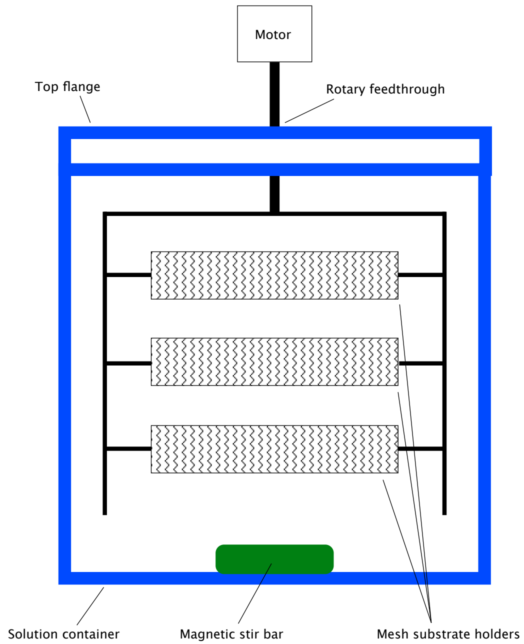


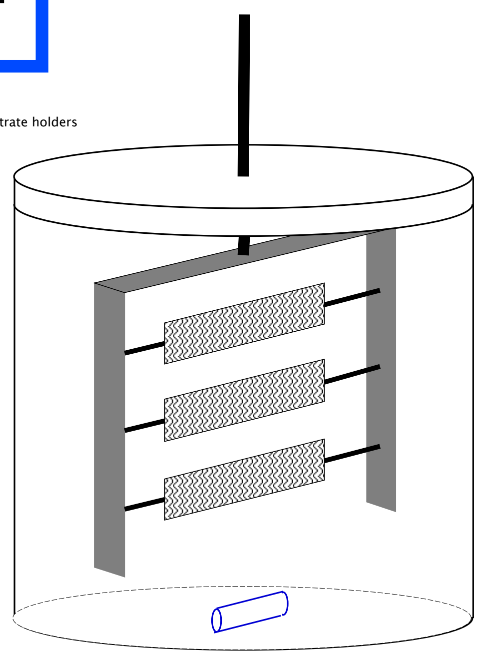
Set 3



- The first sample set shows a relatively high concentration of Pd nodules in the deposit
- Published data show that commercial Pd(dba)$_2$ actually contains varying concentrations of Pd nano/micro-particles *even in the as-received state*
- These particles appear to be deposited with high efficiency relative to molecular species
  - They are therefore depleted from solution after preparation of the first sample set
- Resulting changes in deposit properties can account for (along with depletion of the precursors from solution) the observed set-to-set differences in loading and performance

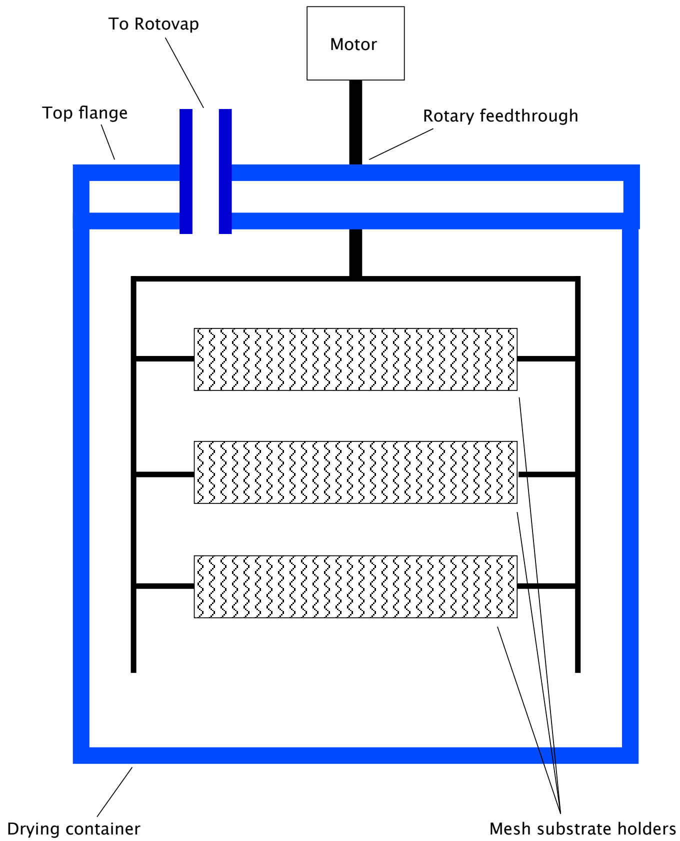
Proof-of-Principle Solution Infiltration System - I





- A proof-of-principle system was designed for infiltrating multiple foam substrates
  - A primary goal is to minimize the ratio of solution volume to substrate volume as much as feasible (waste minimization)
  - Magnetic stirring of solution at the desired frequency
  - Rotation or counter-rotation of substrate holder at the desired frequency
  - The design can easily be generalized to a variety of substrate shapes and sizes

Prototype Solution Infiltration System - II



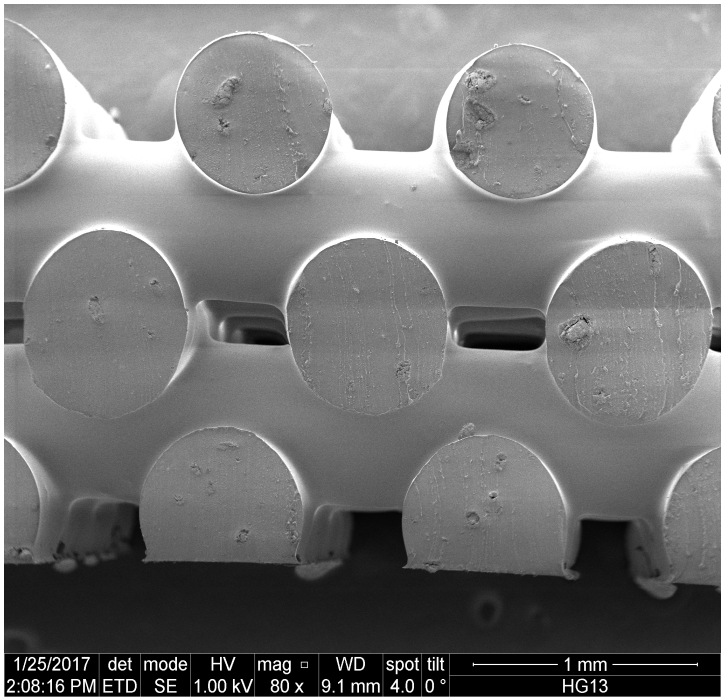
- The substrate holder can be placed into a vacuum drying chamber to quickly remove toluene once the infiltration is complete
- Used solutions can be treated in a Rotovap to recover and recycle the toluene, reducing the environmental footprint of the operation

Solution Infiltration Summary

- The toluene solvent extracts un-polymerized monomer from silicone foams – the resulting mass loss was quantified to enable accurate determination of the getter loading
- The infiltration process appears to be adequately reproducible
- Solution shelf life may be limited – $Pd(dba)_2$ appears to decompose in toluene to Pd particles and free dba – alters deposit characteristics and effective getter capacity
- Solution re-use may (depending on solution concentration) be limited by depletion of the getter/catalysts compounds from solution during infiltration
  - Any Pd particles in the as-received $Pd(dba)_2$ will introduce additional run-to-run variability
- ***A spec must be developed for the acceptable range of getter loading and effective hydrogen capacity per mass of foam***

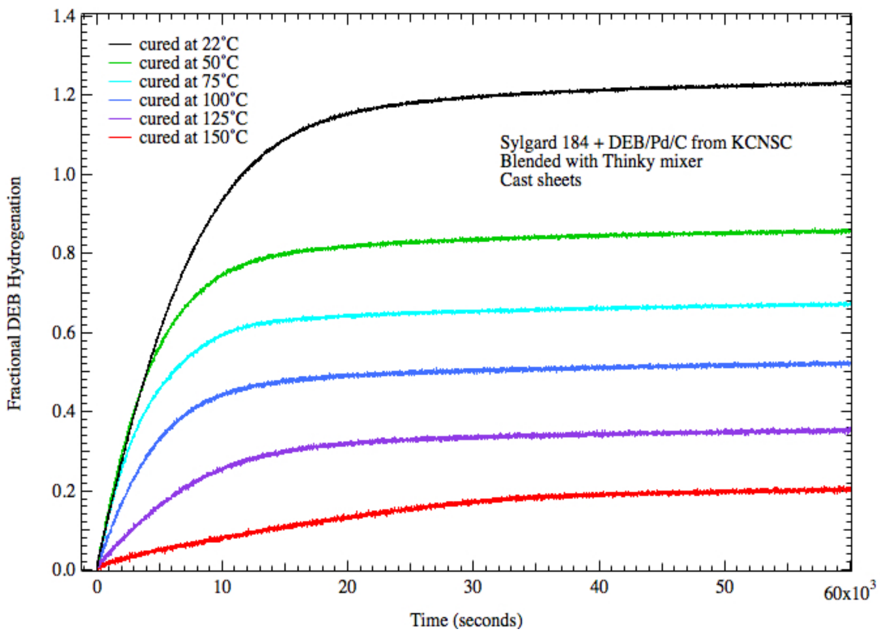
- Proof-of-principle hardware has been designed for infiltrating multiple substrates
- A Rotovap has been purchased to demonstrate recovery of toluene from used solution, enabling recycling of the solvent and reduced waste disposal

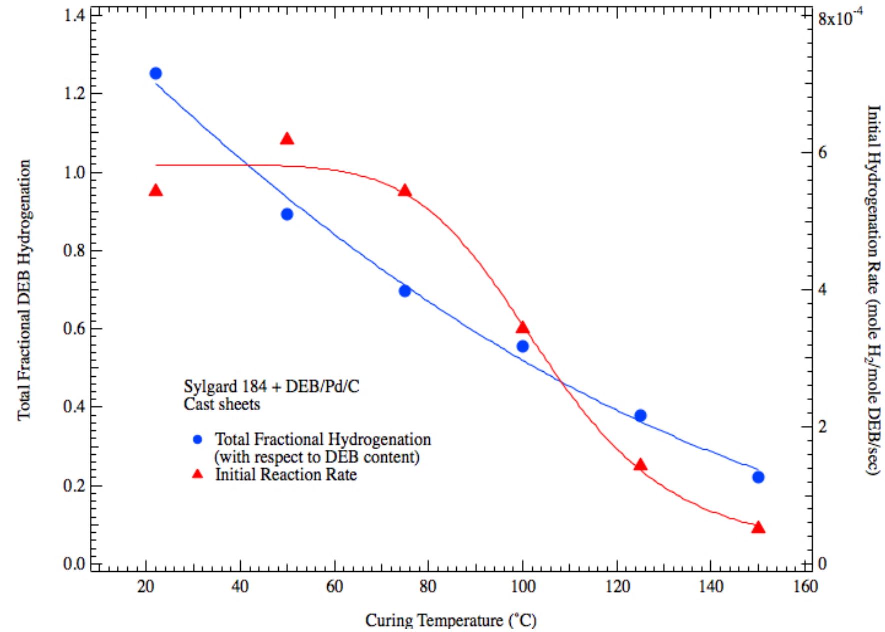
Additive Manufacturing - Concept



- Project to AM precise and reproducible foam structures from silicone/getter composite resins
- Funded through Enhanced Surveillance WP
- Collaboration with Denisse Ortiz-Acosta of C-CDE, who is the project lead
- Work is relevant to Readiness as well
- Primary MST-7 responsibility is to characterize the performance of composite resins in both cast and printed forms
- Experiments have so far been primarily based on Sylgard 184 resin loaded with 4.0-4.3 wt% DEB plus Pd/C or Pd(dba)$_2$ as catalyst

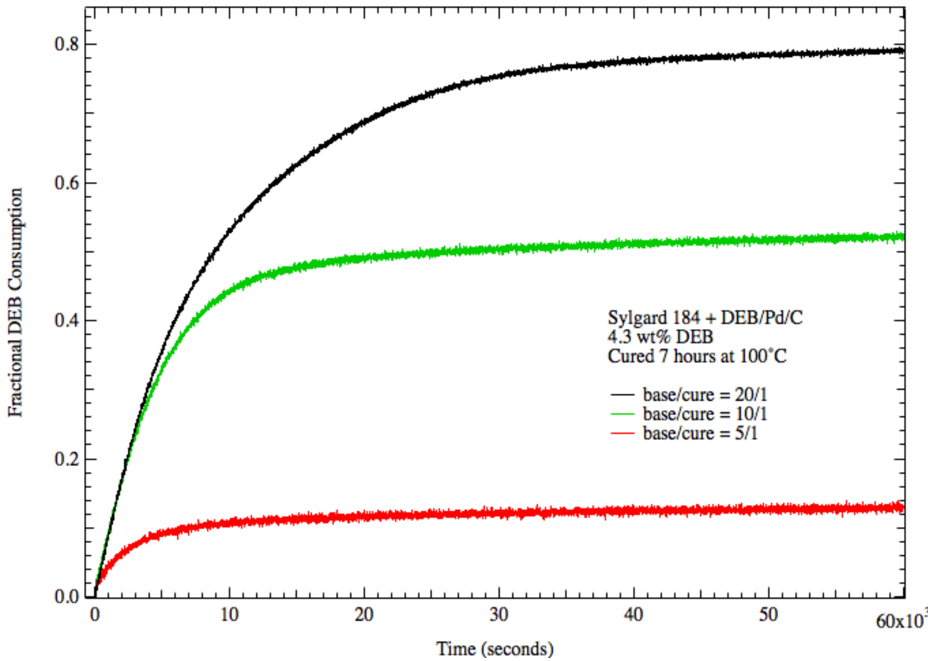
Effect of Curing Temperature

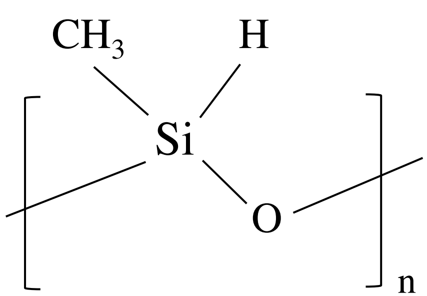




- Silicone/getter composites are capable of excellent performance
  - Diffusion of hydrogen through the silicone matrix is not a major constraint
- High cure temperature is desired for AM in order to shorten cure time
  - Reduce part deformation and enable smaller feature size
- However, increasing cure temperature is found to dramatically reduce the effective hydrogen capacity and, especially at higher values, the reaction rate
  - T_{cure} = 75˚C was found to provide an acceptable compromise

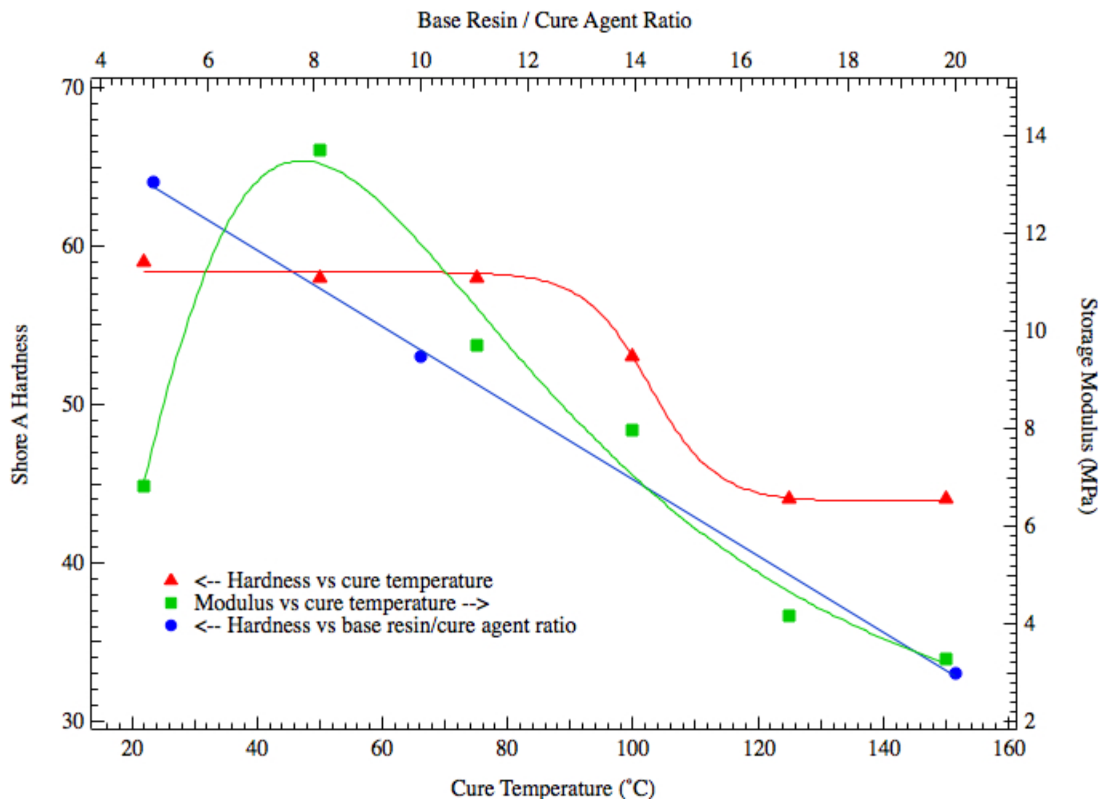
Effect of Cure Agent Concentration





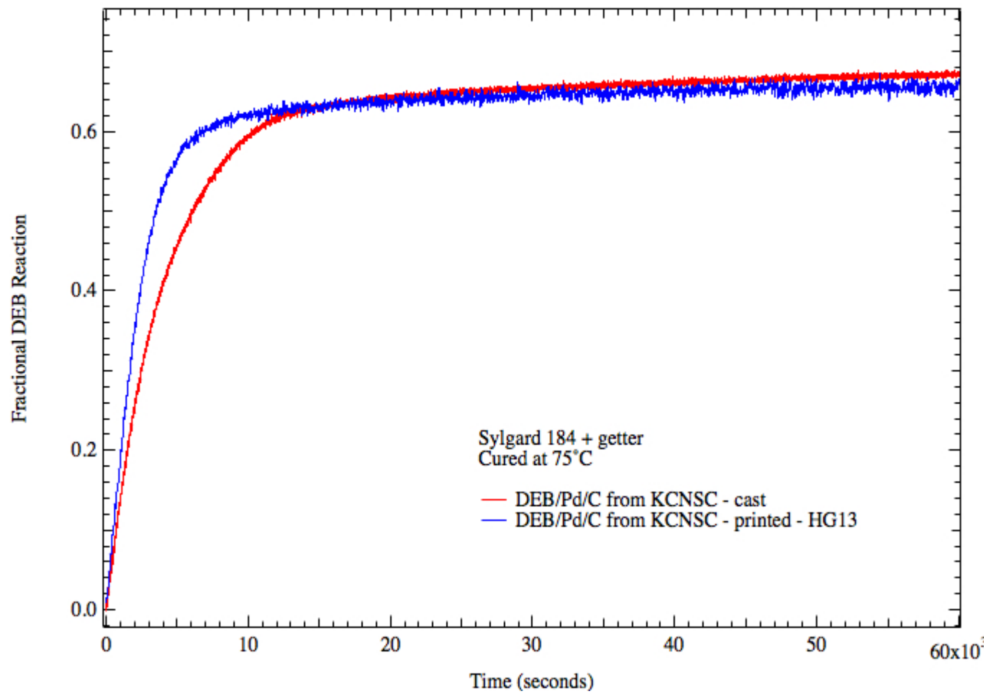
- At fixed T_{cure}, an increase in cure agent concentration is also found to dramatically degrade getter performance
- Suggests reaction between DEB and a component of the cure agent during the cure process, decreasing the concentration of active getter sites
  - Confirmed by NMR measurements
- It is thought that reaction occurs with the methylhydrogen siloxane component of the cure agent
  - Nominal concentration is 2-3 wt%
    - Comparable to DEB concentration

Effect on Mechanical Properties



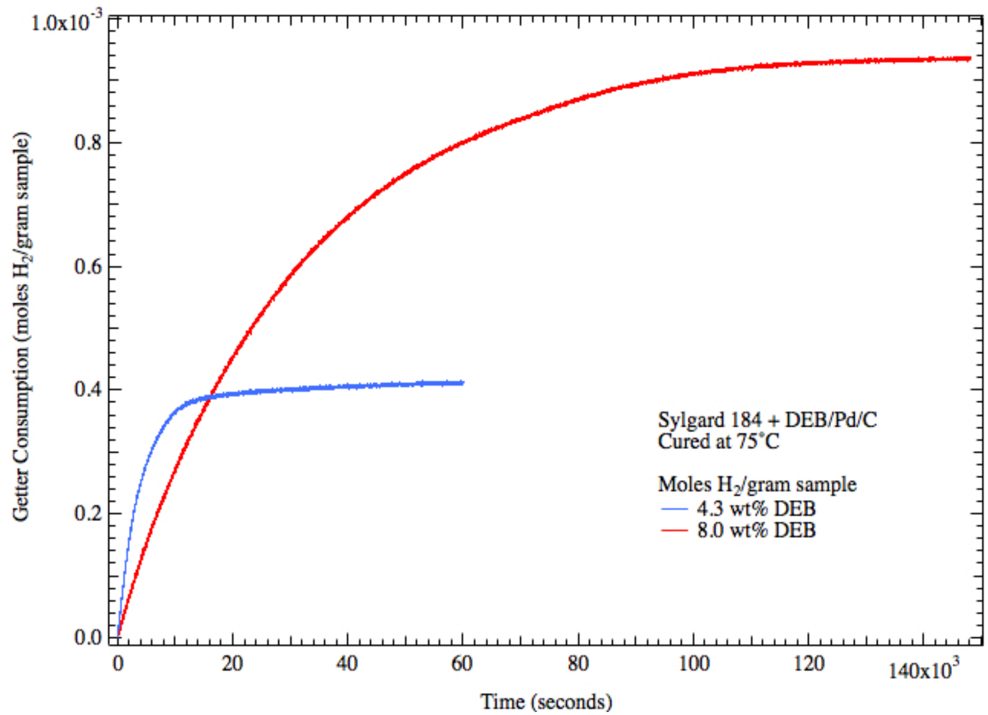
- Reaction between methylhydrogen siloxane and DEB during curing reduces the crosslink density of the cured sample
- This in turn causes a significant degradation of the mechanical properties
- The degradation may or may not be important depending on the application

Cast vs. Printed Samples



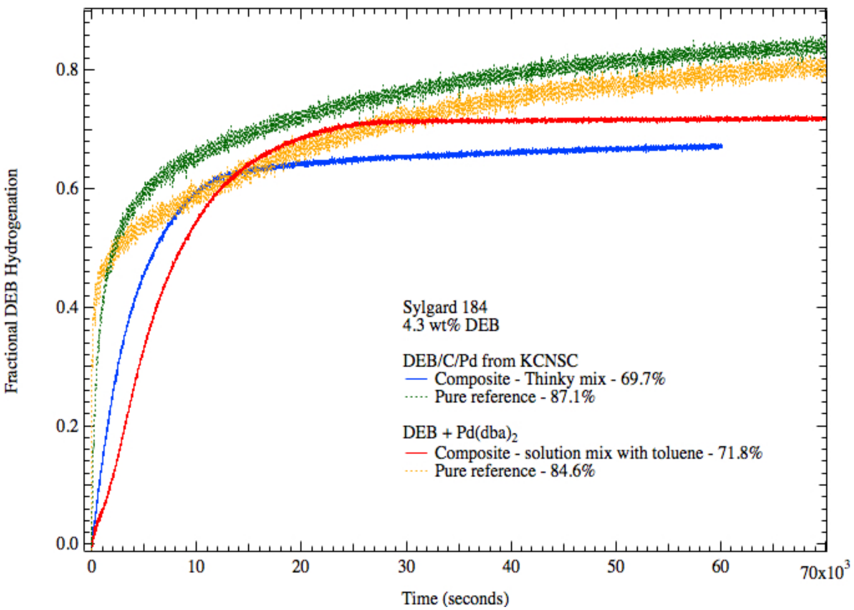
- Silicone/getter composite resins have been successfully printed
- The effective hydrogen capacity of the printed samples is essentially equal to that of cast samples
  - No deleterious effects caused by the printing process
- Initial reaction rate is higher for the printed samples
  - Higher specific surface area

Effect of DEB Concentration

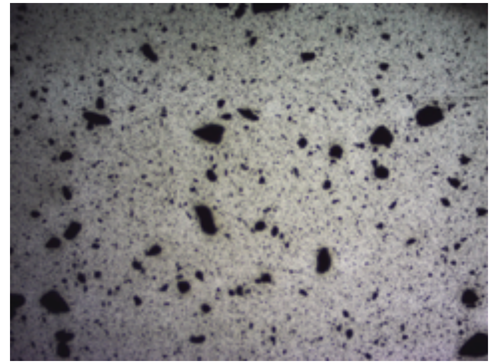


- Preliminary experiments on cast samples demonstrate that the hydrogen capacity of the composite can be effectively increased by increasing the DEB/Pd/C concentration
- Loss of capacity caused by the reaction of DEB during curing can be easily recovered
- Printing has not yet been demonstrated – changes to resin rheology may have an influence but can be accounted for by adjusting inert filler concentration

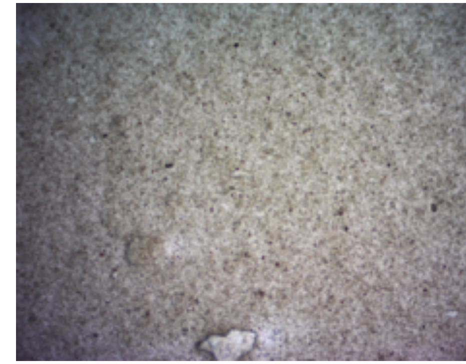
Effect of Catalyst



Pd/C



Pd(dba)$_2$



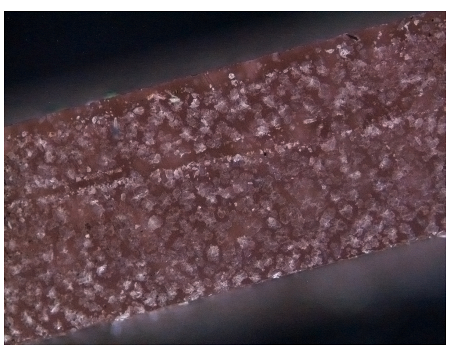
- Composite resins were also prepared using Pd(dba)$_2$ as the catalyst
  - Solution blending with toluene
  - More uniform dispersion of catalyst and getter
  - Fewer large aggregates in the resin
    - Less clogging of printer nozzle
    - Finer feature size
- Performance of Pd(dba)$_2$ is essentially equivalent to that of Pd/C
- AM printing of this resin has been demonstrated

Solution Infiltration of AM Samples

- Back-up process in case printing a Sylgard/ getter composite resin was not possible
- Maintain benefits of precision AM structure

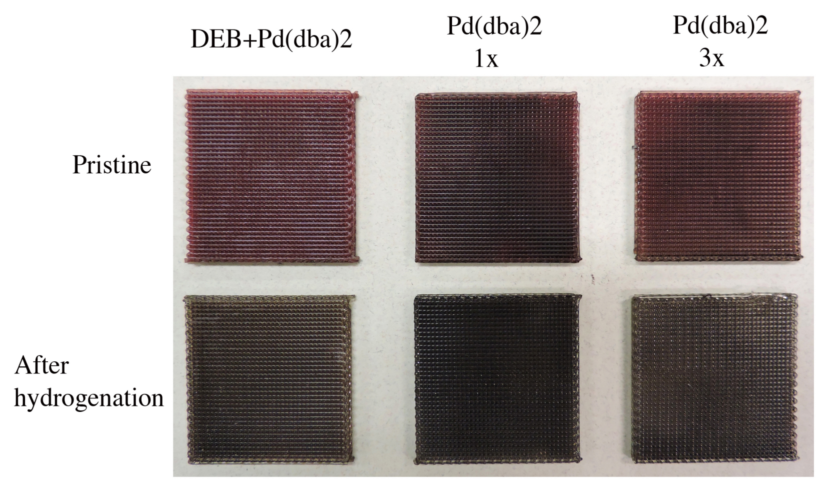
- Substrates (three in each set)
  - AM Sylgard 184 mesh
  - Cast Sylgard 184 sheet (2 mm thick)
- Solution #1
  - 2.40e-2 M DEB
  - 4.67e-3 M $Pd(dba)_2$
  - Mole ratio DEB/$Pd(dba)_2$ = 5.14

- Material completely infiltrated 2 mm thick cast sample – aided by swelling of silicone matrix by the toluene solvent

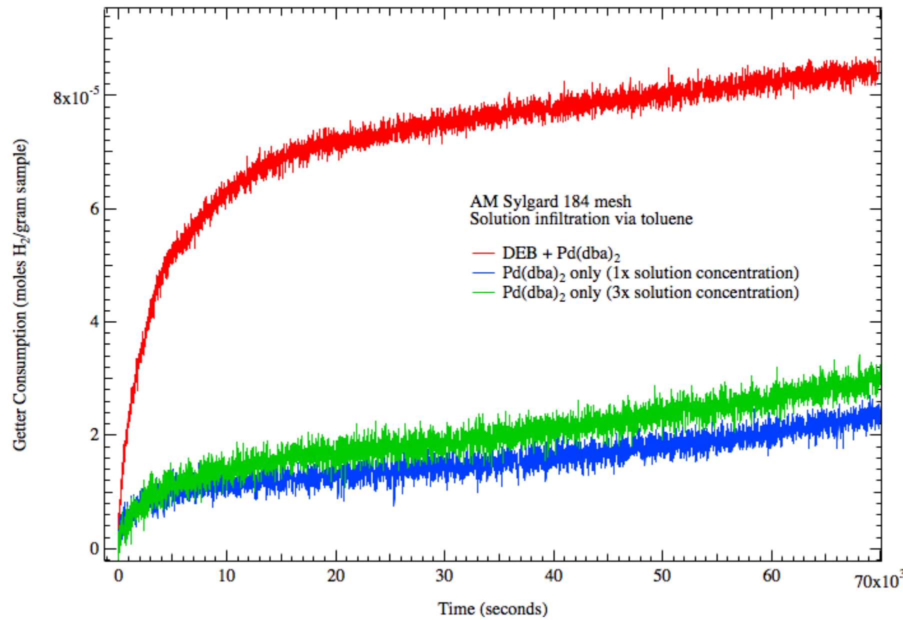


- Samples from Set #1 appears red/purple – the color of $Pd(dba)_2$ → Did DEB successfully infiltrate as well?
  - Additional samples with only $Pd(dba)_2$ prepared as a test (compare performance with nominal DEB + $Pd(dba)_2$)

- Solution #2
  - 4.67e-3 M $Pd(dba)_2$
- Solution #3
  - 1.40e-2 M $Pd(dba)_2$



Infiltrated AM Samples - Performance



- Extrapolated reaction extent for DEB/Pd(dba)$_2$ is 9.81e-5 mole H_2/g sample
- Corresponding value for Set #2 is ~2-3e-5 mole H_2/g sample
  - Both DEB and Pd(dba)$_2$ *are* infiltrated with more or less comparable efficiency
- Set #3 shows relatively little gain in performance
  - Pd(dba)$_2$ infiltration appears to reach a saturation point

- Printed samples with KCP material hydrogenate 3.81e-4 mole H_2/g sample (3.9x better)
- Because printing of the composite resin has been demonstrated, this is not likely to be a needed alternative process

AM Summary

- Silicone + DEB/Pd/C composites act as effective getter materials – diffusion of hydrogen through the silicone is not a significant limitation
- DEB reacts with methylhydrogen-siloxane in the cure agent during curing, consuming an increasing fraction of getter sites as T_{cure} is increased
- This reaction also reduces crosslinking during cure, degrading mechanical properties
  - T_{cure} = 75˚C represents a suitable compromise
- Getter capacity can be improved by increasing the DEB/Pd/C concentration in the resin
- AM printing of 3D mesh structures from the composite resin has been demonstrated
- Use of $Pd(dba)_2$ as catalyst decreases the size of aggregates in the resin, reducing nozzle clogging and enabling smaller feature size, and has also been demonstrated
- AM structures prepared from silicone only can be treated by solution infiltration of DEB/$Pd(dba)_2$, but the loading is considerably less than AM samples prepared from the silicone/DEB/Pd/C composite resin

Proposed Future Work

Vapor infiltration

- This method presents a number of serious difficulties with respect to scaled-up production
- Overall performance is not as good as materials produced by solution infiltration
- Unless otherwise directed, future work will focus on the solution method

Solution Infiltration

- Attempt to improve the aging and re-use characteristics of the solution with respect to the Pd precursor compound
  - Obtain a better understanding of how $Pd(dba)_2$ ages/decomposes as a function of time in toluene
  - Evaluate modifications to $Pd(dba)_2$ to enhance stability and infiltration reproducibility
  - Evaluate the use of alternative precursors such as $Pd(acac)_2$, which may be more stable in toluene
- Assemble a prototype system to enable processing multiple parts
- Assemble a closed solvent evaporation system to enable capture/recycling of evaporated solvent

Additive manufacturing (C-CDE collaboration funded by Enhanced Surveillance)

- Evaluate alternate matrix polymers
- Evaluate alternate getter compounds, including a matrix polymer functionalized with getter sites